Dispersion of quantum well states in Cu/Co/Cu(001)

Y. Z. Wu,[1] C. Y. Won,[1] E. Rotenberg,[2] H. W. Zhao,[1,3] F. Toyoma,[1] N. V. Smith,[2] and Z. Q. Qiu,[1,4]
[1]*Department of Physics, University of California, Berkeley, California 94720*
[2]*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720*
[3]*International Center for Quantum Structures, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*
[4]*Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720*
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Quantum well states (QWS's) in Cu thin films grown on Co/Cu(001) were studied using angle-resolved photoemission spectroscopy. For the normal photoemission, QWS's from both lower and higher energy bands relative to the vacuum level were measured, and explained by phase accumulation method. QWS's from the lower band were studied in detail as a function of the in-plane momentum $k_{\parallel}$. We found that the QWS dispersion depends on the Cu film thickness. From the experimental data, we deduced the quantized perpendicular momentum $k_{\perp}$ and the energy as a function of $k_{\parallel}$. Our results show that the in-plane effective mass can not be obtained by a simple parabolic fitting of the E vs $k_{\parallel}$ due to the dependence of $k_{\perp}$ on $k_{\parallel}$.

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I. INTRODUCTION

Electrons inside a metallic thin film experience confinement in the normal direction of the film to form quantum well states (QWS's).[1] There has been a great interest recently to study the QWS's and the associated new properties in low-dimensional systems. It was found that QWS's play a key role in a number of important phenomena such as the oscillatory interlayer coupling,[2,3] the magnetic anisotropy,[4] and the stability of magic thickness,[5] etc. For QWS's below the Fermi level (E_F), photoemission provides the most direct measurement. In particular, the QWS in the normal direction of the film ($k_{\parallel}=0$) has been well studied and can be understood quantitatively by the so-called phase accumulation method (PAM).[6–8] One striking feature associated with QWS's in metallic thin films is that the QWS energy below the vacuum level *increases* with the film thickness due to the envelope modulation of the electron wave function by the lattice potential.[9] This result implies that QWS energy should *decrease* with the film thickness for the energy band above the vacuum level because of its opposite *E-k* dispersion as compared with that below the vacuum level. This is the first issue we will discuss in this paper.

Another issue we will address is the QWS off the normal direction. In the Cu/Co/Cu(001) system, which is one of the representative systems for QW study, QWS's off the normal direction were studied in detail only near the neck of the Fermi surface because of its relation to the short period oscillations of the interlayer coupling.[10] Curti *et al.* found that the dispersion of QWS's is strongly influenced by the energy gap of the substrate, and exhibits a flat dispersion near the neck of the Fermi surface.[10] For QWS's near the normal direction, the in-plane dispersion was usually used to determine the in-plane effective mass of the electron using a parabolic fitting. It was found that the in-plane effective mass in the Ag(111) system has a strong dependence on the substrate as well as the binding energy.[11,12] To our best knowledge, the dispersion of QWS's in Cu/Co/Cu(001) has not been studied in detail. Since the energy gap of the Co substrate depends on the in-plane momentum,[10] one has to be careful in obtaining the in-plane effective mass from the parabolic shape of the QWS dispersion near the normal direction. As we show in this paper, a little change in $k_{\perp}$ has a dramatic effect on the dispersion of the QWS. Therefore a simple fitting to the parabola QW dispersion will not give the correct in-plane effective mass.

In this paper, we report the QWS study using angle-resolved photoemission spectroscopy (ARPES) for the Cu/Co/Cu(100) system. First, QWS's in the normal direction were studied for both the lower and upper energy bands relative to the vacuum level. Using the PAM model, we can describe the QWS in both bands as a whole. Second, QWS's with different in-plane momentum were studied near the normal direction. We found that the QWS dispersion depends on the Cu film thickness and that the quantized $k_{\perp}$ changes with the in-plane momentum $k_{\parallel}$. The latter has a dramatic effect on obtaining the in-plane effective mass of the electron.

II. EXPERIMENT

A Cu(001) single crystal was prepared by mechanical polishing down to 0.25-μm diamond paste followed by electrochemical polishing.[13] Then the Cu substrate was cleaned *in situ* with cycles of Ar ion sputtering at 1.5 keV and annealing at 600–700 °C. The Co and Cu films were grown at room temperature by molecular-beam epitaxy. The growth rate was measured by a quartz crystal oscillator. The base pressure was about 1×10^{-10} torr, and the pressure during the growth was about 1.4×10^{-9} torr. An 8-monolayer (ML) Co film was grown on Cu(001) to serve as the ferromagnetic substrate. Then a Cu wedge of a slope of ~5 ML/mm was grown for the QWS study.

X-ray photoemission measurement was performed at beamline 7.0.1.2 of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory. The small beam size (~50 μm) gave a thickness resolution ~0.3 ML on the wedged sample. 83-eV photon energy was used to select the electronic states near the belly of the Cu Fermi surface. The photoemission electrons were collected by a Scienta SES-100 analyzer which simultaneously measures the energy

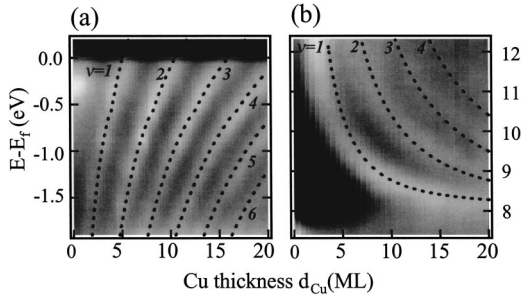

FIG. 1. Photoemission intensity normal to the film surface ($k_{\parallel}=0$) as a function of the Cu film thickness and the electron energy. (a) Lower band below the Fermi level. (b) Upper band above the vacuum energy level. The dotted curves are calculated results from the PAM.

and angular spectra. The angular resolution of the detector is ~0.2°. To measure the QWS above the vacuum level, secondary low-energy electrons were measured with a negative 40-V voltage applied to the sample to accelerate the emission electrons.

III. RESULTS AND DISCUSSION

A. Normal photoemission

The Cu energy bands along the ΓX direction with Δ_1 symmetry consists of two *sp* bands near the vacuum level with the lower band crossing the Fermi level and the upper band ~8 eV above the vacuum level.[14–16] These two bands come from band folding with an energy gap opening at the Brillouin-zone (BZ) boundary. Electrons from both bands should experience quantum confinement due to the presence of the minority spin energy gap of the Co film. Figure 1(a) shows the photoemission intensity as a function of the electron energy below E_F and the Cu film thickness. Similar to our previously reported result, the energy increases with the Cu thickness with ~5.6-ML oscillation periodicity at E_F. Because the upper band is above the Fermi level, measurement of the unoccupied states is needed. Angle-resolved inverse photoemission spectroscopy (ARIPES) is usually used to measure the unoccupied states, but it is not efficient for states too far above E_F. For states far above E_F, especially above the vacuum level (e.g., the Cu upper band in this paper), angle-resolved secondary electron emission spectroscopy (ARSEES) has been employed. For example, Law *et al.* used ARSEES to determine the energy band of graphite up to 20 eV above E_F which is not accessible by inverse photoemission.[17] To eliminate the influence of the residual magnetic field on the low energy emission electrons, a negative voltage is usually applied to the sample to accelerate the emission electrons though this may sacrifice a little bit of the angular resolution. In fact, such method was successfully used to determine the Cu energy at the X_1 point[15] as well as the QWS in the Cu/Co/Cu(001) system.[18] Figure 1(b) shows the photoemission intensity using such experimental method. The QWS of the upper band can be clearly seen as a function of energy and the Cu thickness. The energy of the QWS decreases with the Cu thickness, which is opposite to the behavior of the QWS of the lower band. This can be qualitatively explained by the opposite *E-k* dispersion of these two energy bands. Another feature associate with the upper band QWS is that the QWS energy approaches a particular energy level at thicker Cu thickness. This energy corresponds to the upper edge of the energy gap at the BZ boundary for bulk Cu.

To quantitatively understand the QWS from these two bands as a whole, we calculate the position of the QWS using the phase accumulation method[6] in which the quantization condition is given by

$$2k_{\perp}^{\mathrm{eff}}d_{\mathrm{Cu}}-\phi_C-\phi_B=2\pi\nu, \quad \nu=\text{integer number}. \tag{1}$$

Here $k_{\perp}$ is the electron momentum along the [001] direction, and $k_{\perp}^{\mathrm{eff}}=k_{\mathrm{BZ}}-k_{\perp}$ is the effective momentum with k_{BZ} being the BZ vector. ϕ_B and ϕ_C are the phase gains of the electron wave function upon reflection at the Cu/vacuum and Co/Cu interfaces, respectively. We use the same expression in Smith *et al.* to calculate ϕ_B and ϕ_C.[6] Since the Cu electrons are confined by Co minority spin band gap, we take the upper (E_U) and lower (E_L) energies of the potential well from the energy gap of the Co minority spin band along the [001] direction (for the lower band, $E_U=-0.58$ eV, $E_L=3.9$ eV; for the upper band, $E_U=9.6$ eV, $E_L=2.5$ eV).[16] The nearly free-electron model is used to describe the *E-k* dispersion for both the lower and the upper energy bands, i.e.,

$$E(k)=\frac{\varepsilon_k+\varepsilon_{k-2k_{\mathrm{BZ}}}}{2} \pm\sqrt{\left(\frac{\varepsilon_k-\varepsilon_{k-2k_{\mathrm{BZ}}}}{2}\right)^2+\left(\frac{E_g}{2}\right)^2} \quad \text{with} \quad \varepsilon_k=\frac{\hbar^2k^2}{2m_{\perp}^*}. \tag{2}$$

Here E_g is the energy gap at the BZ boundary, and $m_{\perp}^*$ is the effective mass of the electron along the normal direction. The "+" and "−" signs in Eq. (2) represent the upper and lower energy bands, respectively. The Fermi wave vector k_F can be obtained from the QW oscillation periodicity at the E_F in Fig. 1(a), i.e., $\pi/|k_{\mathrm{BZ}}-k_F|=5.6$ ML. This yields the value of $k_F=1.43$ Å^{-1} which is very close to the literature value of 1.44 Å^{-1}.[19] Using Eqs. (1) and (2), we fitted the photoemission data for both the upper and lower energy bands with E_g and $m_{\perp}^*$ as the fitting parameters. The fitting (dashed lines in Fig. 1) agrees reasonably well with the experimental results, and yields the values of $E_g=6.8$ eV and $m_{\perp}^*=1.14m_e$ (m_e is the free-electron mass). This proves that the nearly free-electron model and the PAM describes reasonably well the QWS along the normal direction for both the lower and upper energy bands.

B. QWS dispersion and in-plane effective mass

The in-plane dispersion of the QWS was measured using ARPES around the normal direction of the film. Figure 2 shows the typical spectra as a function of the energy and the

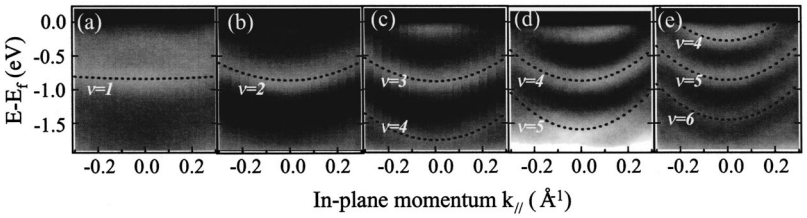

FIG. 2. The QWS energy versus the in-plane momentum $k_\parallel$ at different Cu thickness: (a) 3.3 ML, (b) 7.1 ML, (c) 10.3 ML, (d) 15.2 ML, and (e) 19.6 ML. The dashed lines are results of parabolic fitting, and ν is the QW index.

in-plane momentum at several Cu thicknesses. The QWS index ν was labeled in Fig. 2. There are several characteristics that can be seen immediately. First, all QWS's exhibit parabolic shape dispersion as a function of the in-plane momentum $k_\parallel$. Second, the QW dispersion depends strongly on the Cu film thickness. For example, the QWS's exhibit nearly flat dispersion below 4-ML Cu and gradually develop into the parabola shape as the Cu thickness increases. This trend can be clearly seen for QWS's near the energy of -0.85 eV at different Cu thickness. It should be mentioned that the observed flat dispersion below 4-ML Cu is not associated with the Co *d* band whose energy is above -0.85 eV.

The quadratic dependence of the QW energy on $k_\parallel$ can be mathematically expressed as

$$E(k_\parallel)=E_0+\hbar^2k_\parallel^2/2m_\parallel^{*\mathrm{fit}}. \tag{3}$$

In the literature, E_0 and $m_\parallel^{*\mathrm{fit}}$ are used as fitting parameters and the fitting result of $m_\parallel^{*\mathrm{fit}}$ was interpreted as the electron in-plane effective mass.[11,12,20] Following the literature, we performed the fitting (dashed lines in Fig. 2) in the range of $-0.3<k_\parallel<0.3$ Å^{-1} and obtained the value of $m_\parallel^{*\mathrm{fit}}$ for all the QWS's [Fig. 4(b)]. The flat dispersion in Fig. 2(a) for Cu thickness below 5 ML yields a value of $m_\parallel^{*\mathrm{fit}}$ at least greater than $10m_e$. For other QWS's, the mathematical uncertainty of the $m_\parallel^{*\mathrm{fit}}$ fitting is about $\pm5\%$. The value of $m_\parallel^{*\mathrm{fit}}$ obtained in this way decreases with the Cu thickness.

The good fitting in Fig. 2 proves the quadratic dependence of the QWS energy on the $k_\parallel$. Such quadratic relation can also be argued from the symmetry of the (001) surface that the QWS energy should be invariant with respect to the action of $k_\parallel$ to $-k_\parallel$ so that to the lowest order expansion the QWS energy should depend quadratically on $k_\parallel$. Therefore Eq. (3) should be correct phenomenally. However, the assignment of the fitting parameter $m_\parallel^{*\mathrm{fit}}$ to the electron in-plane effective mass actually preassumed that $k_\perp$ does not vary with $k_\parallel$. This assumption is correct only when the phase ϕ_C and ϕ_B do not depend on $k_\parallel$ [see Eq. (1)]. As pointed out in Ref. 10, the Co energy gap varies with the in-plane momentum, and thus the phase ϕ_C and $k_\perp$ in Eq. (1) should change accordingly. Therefore the good fitting results in Fig. 2 only prove that Eq. (3) is a correct phenomenological formula, it does not guarantee that $m_\parallel^{*\mathrm{fit}}$ equals the electron in-plane effective mass $m_\parallel^*$, i.e., $m_\parallel^{*\mathrm{fit}}$ should be treated only as a mathematical fitting parameter.

To explore the connection between the fitting parameter $m_\parallel^{*\mathrm{fit}}$ in Eq. (3) and the electron in-plane effective mass $m_\parallel^*$, the following general formula should be used:

$$E(k_\perp,k_\parallel)=\hbar^2k_\perp^2/2m_\perp^*+\hbar^2k_\parallel^2/2m_\parallel^* \tag{4}$$

with $k_\perp$ depending on $k_\parallel$ and $m_\perp^*=1.14m_e$ (see Sec. III A).

Thus with Eq. (4) and the phenomenological formula Eq. (3), it is easy to show that

$$k_\perp^2=2m_\perp^*E_0/\hbar^2+m_\perp^*(1/m_\parallel^{*\mathrm{fit}}-1/m_\parallel^*)k_\parallel^2$$

$$\text{or}\quad k_\perp\approx k_\perp^0+m_\perp^*(1/m_\parallel^{*\mathrm{fit}}-1/m_\parallel^*)k_\parallel^2/2k_\perp^0, \tag{5}$$

where $k_\perp^0$ is the value of $k_\perp$ at $k_\parallel=0$. It is clear that $m_\parallel^{*\mathrm{fit}}=m_\parallel^*$ only when $k_\perp$ does not depend on $k_\parallel$. Otherwise a quadratic dependence of $k_\perp$ on $k_\parallel$ is expected, and $m_\parallel^{*\mathrm{fit}}\neq m_\parallel^*$.

To obtain the in-plane effective mass correctly, we need to determine the $k_\perp$ as a function of $k_\parallel$ experimentally. This was done by two steps. First, we measure the QWS versus the Cu thickness at different in-plane momentum $k_\parallel$ (Fig. 3). The value of $k_\perp$ at any given energy can be obtained from the thickness oscillation periodicity of the QWS [see Eq. (1)]. This procedure basically determines the E-$k_\perp$ relation (energy band) at different in-plane momentum $k_\parallel$. Figure 3(d) shows the E-$k_\perp$ relation obtained in this way at three representative $k_\parallel$ values. Second, for a given QWS of index ν in Fig. 2, we trace the QWS energy at different $k_\parallel$ and obtain the corresponding $k_\perp$ value from the E-$k_\perp$ relation of the first step. In this way, we determined the $k_\perp$-$k_\parallel$ relation for QWS of index ν. Figure 4(a) shows $k_\perp$ versus $k_\parallel$ for several QWS's with similar energies ($E\sim-0.85$ eV). The reason to

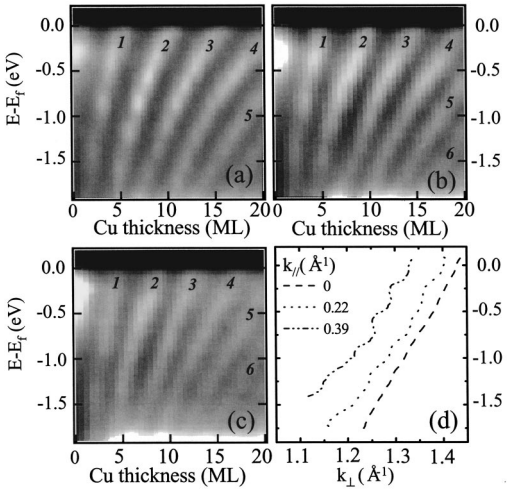

FIG. 3. (a)–(c) Photoemission intensity as a function of the Cu film thickness and the electron energy at (a) $k_\parallel=0$ Å^{-1}, (b) $k_\parallel=0.22$ Å^{-1}, and (c) $k_\parallel=0.39$ Å^{-1}. (d) The electron energy versus $k_\perp$ (energy bands) obtained from (a)–(c) at the corresponding $k_\parallel$. The numbers are the QW index ν.

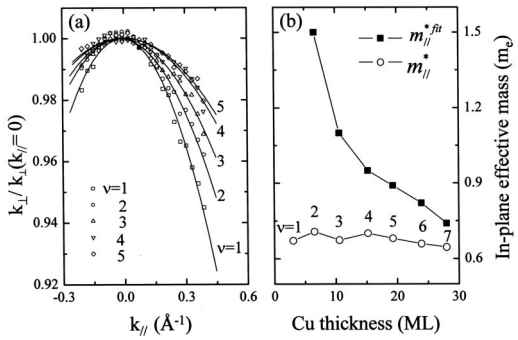

FIG. 4. (a) The normalized wave vector $k_\perp$ as a function of $k_\parallel$ from QWS's with similar energies ($E\sim-0.85$ eV) and different index ν. The solid lines are from parabolic fitting. (b) The in-plane effective mass versus the Cu film thickness. The solid dots are the fitted in-plane effective mass $m_\parallel^{*\mathrm{fit}}$, and the open dots are the in-plane effected mass $m_\parallel^*$ corrected using Eq. (4).

choose the same QW energy is to eliminate the possible energy dependence of the effective mass so that we can compare the $k_\perp$-$k_\parallel$ relation for different index ν. As shown in Fig. 4(a), the $k_\perp$ has different dependence on $k_\parallel$ for different index ν, and the quadratic dependence of $k_\perp$ on $k_\parallel$ [Eq. (5)] can be clearly seen.

After obtaining the $k_\perp$-$k_\parallel$ relation, we can derive the in-plane effective mass $m_\parallel^*$ using Eq. (4). The results of $m_\parallel^*$ for different QW index ν are shown in Fig. 4(b). The results of $m_\parallel^{*\mathrm{fit}}$ from a simple parabola fitting using Eq. (3) are also shown in Fig. 4(b) for comparison. $m_\parallel^{*\mathrm{fit}}$ for $\nu=1$ is omitted because it is too large. Figure 4(b) clearly shows that there is a significant difference between $m_\parallel^{*\mathrm{fit}}$ and $m_\parallel^*$. From the analysis above, this difference comes from the dependence of $k_\perp$ on $k_\parallel$. It is interesting to note that a small variation in $k_\perp$ could cause a big difference between $m_\parallel^{*\mathrm{fit}}$ and $m_\parallel^*$. For example, $\sim$4% change in $k_\perp$ causes $\sim$50% difference between $m_\parallel^{*\mathrm{fit}}$ and $m_\parallel^*$ for $\nu=2$ QWS, and the $\nu=1$ QWS effective mass $m_\parallel^*$ is about $0.67m_e$ though the QW dispersion is virtually flat. Another fact is that the $m_\parallel^{*\mathrm{fit}}$ decreases with the Cu thickness, but the corrected effective mass $m_\parallel^*$ varies little with the Cu thickness.

C. Discussion

Our experimental results show that one has to be careful in analyzing the QW dispersion to obtain the electron in-plane effective mass. The reason is that the quantized $k_\perp$ varies with $k_\parallel$. $k_\perp$ would be independent of $k_\parallel$ if the QW potential barrier were infinitely high, but such a situation does not occur when a substrate provides the QW potential. In fact, such effect from the substrate has already been observed in experiments where the in-plane QW dispersion is significantly different for thin films of the same element grown on different substrates.[11,12] Electronic hybridization at the interface between the QW thin film and the substrate was suggested to account for the above observations.

For the case of Cu/Co/Cu(001), tight binding calculation shows that the minority spin energy gap of the fcc Co decreases with increasing $k_\parallel$ and crosses zero at $k_\parallel \sim 0.45$ Å^{-1}.[10] From the PAM, the phase ϕ_C at the Cu/Co interface depends on the Co energy gap, and thus a variation of the Co energy gap with $k_\parallel$ should change the quantized $k_\perp$ accordingly. Noting that the QW phase changes from zero to $-\pi$ as the energy changes from the upper to the lower edges of the substrate energy gap, the value of ϕ_C at the same energy should decrease as the Co energy gap decreases with $k_\parallel$. On the other hand, both ϕ_C and ϕ_B increase with the energy [see Eqs. (2) and (3)] in Ref. 3. The overall change of $k_\perp$ as a function of $k_\parallel$ depends on the competition between the Co gap variation and the QW energy change. Nevertheless, the dependence of $k_\perp$ on $k_\parallel$ should have the same trend for all QW indexes ν.

IV. SUMMARY

The QWS's in the Cu/Co/Cu(001) system were studied using ARPES. For the normal photoemission, QWS's from both the lower and upper bands were measured and explained using the PAM. The QWS dispersion as a function of the in-plane momentum $k_\parallel$ was investigated in detail. Our results show that the in-plane electron effective mass cannot be obtained by a simple parabolic fitting. The dependence of $k_\perp$ on $k_\parallel$ has to be considered to abstract the correct in-plane effective mass.

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